CO_2 capture by hydrate formation in quiescent conditions: in search of efficient kinetic additives

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Abstract

As a preliminary step to the development of a CO2 capture process under high pressure conditions, an experimental kinetic study of CO2 hydrate formation has been carried out in a high-pressure batch reactor, using as water-soluble additives a mixture of tetrahydrofuran (THF) and surfactant (sodium dodecyl sulfate, SDS). Used together and in suitable concentrations, these two additives were found to be very efficient for promoting CO2 capture.

Keywords: CO2 capture, gas hydrate, kinetic promoters, additives

1. Introduction

Among the spectrum of measures that will have to be developed to fight global warming, carbon and capture sequestration (CCS) technology is seems by many as important options of mitigation of climate change. Although CCS technology appears attractive regarding various GHG emission scenarios [1], the widespread deployment of this technology is limited by the cost of the CO2 capture step.

There are many technical options for CO2 capture or separation based on various technologies as chemical/physical absorption, physical adsorption, cryogenic fractionation and separation via membranes [2]. However, these options suffer from limitations such as high costs, insufficient capacity, technical problems (e.g. corrosion in absorption processes), large energy consumption and important amount of chemicals used [3]. Accordingly, intensive R&D efforts have to be performed in three directions: (i) improving current separation

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techniques and technologies, (ii) reducing the overall cost by lowering both the energy demand and the capital cost requirements, (iii) and develop new approaches and innovative CO2 capture processes. An innovative CO2 capture and separation process using the formation and dissociation of clathrate hydrates is one of them.

Clathrate hydrates are solid crystalline compounds consisting of a lattice-like structure formed by a water network which encages individual guest molecules of suitable size and shape.The water molecules are linked together by hydrogen bonding with the guest molecule stabilizing the entire structure. Theses compounds are formed at moderately low temperatures (a few degrees above 0 °C) and pressures in the range of a few MPa [4]. CO2 capture by gas hydrates is thus considered a promising alternative to classical separation processes, particularly in applications where separation has to be done with an inlet gas at high pressure [5], such as a production gas. Thus, if we consider the whole CCS chain, this separation technique could be economically competitive in comparison with other separation processes which must operate at lower pressure, because it avoids or limits the costs of the recompression step required for injection and storage in the geological reservoir. However, important limitations still have to be unlocked to foresee at industrial scale a viable CO2 capture process by hydrate formation, such as the CO2 selectivity and the slow enclathration kinetics [6]. Accordingly, and in spite of existing published works in these domains [7, 8], we have chosen to address, in priority, these two key directions in our research. In this paper, results relative to kinetics studies with pure CO2 are presented.

Hydrate formation rate being strongly dependent on thermodynamic conditions (for phase equilibria data, see Sloan and Koh (2008) [9]), an interesting option to enhance kinetics is to force the system to operate at higher pressure and/or lower temperature than the equilibrium conditions or, equivalently, to displace the equilibrium conditions to lower pressures and/or higher temperatures by using additives referred to as *thermodynamic promoters*. These promoters are often volatile organic liquids [10] or quaternary ammonium salts [11]. Among them, tetrahydrofuran (THF) has proved to perform very well [12]. Another class of additives, referred to as *kinetic promoters*, are used at low dosage and have no effect on the equilibrium conditions. They consist of surfactant molecules, such as sodium dodecyl sulfate (SDS), which has excellent kinetic promoting effects for hydrocarbon hydrate formation, even under quiescent conditions [13, 14]. Nevertheless, the mechanisms by which these promoters increase the hydrate formation rate are still debated [15, 16].

The absence of mechanical agitation presents many advantages. First, this prevents any gas leakage problem through the agitator gland packing, as the reactor is still maintained under pressure during reaction, and the gas used can be potentially hazardous and flammable. In addition, the energy required to produce sufficient mechanical stirring is not compatible with the development of a cost-competitive CO2 capture process. Recently, Linga *et al.* (2010) [7] obtained significant gas uptake and separation efficiency at lab-scale by stirring with a gas-inducing mechanical agitation system. However, the authors concluded that "if the hydrate process is to be scaled up and used industrially, then the hydrate crystallisation must be carried out without mechanical agitation" [7]. Therefore, for technological, safety and economical reasons, we have chosen to work in quiescent conditions during hydrate formation.

We are not aware of any kinetic (surfactant) promoter of CO2 hydrate formation in batch reaction conditions. In our laboratory, we have made a series of unsuccessful attempts to find such kinetic promoters by using the experimental setup described in this study. However, Liu *et al.* (2008) [17] recently showed that the combination of a surfactant (SDS) and a small amount of a thermodynamic promoter (THF) might be promising in this respect, but just only one concentration of SDS and THF was investigated in their study. This paper further investigates the potentialities of this combination of additives for enhancing the CO2 hydrate capture.

2. Experimental

2.1. Materials

Table 1 reports the chemicals used in this work, suppliers and purities. Solutions were all prepared with ultra-pure water (UPW) having a resistivity of 18.2 mΩ.cm, produced in our laboratory by a PureLab Classic® from ELGA Labwater.

Table 1. Suppliers and purities of materials used.

Chemical	Supplier	Purity
carbon dioxide	Linde gas	99.995 %
sodium dodecyl sulfate (SDS)	Fluka	> 97 %
tetrahydrofuran (THF)	Sigma-Aldrich	> 99.9 %

2.2. Apparatus

The experimental rig used in this work is described in Figure 1.

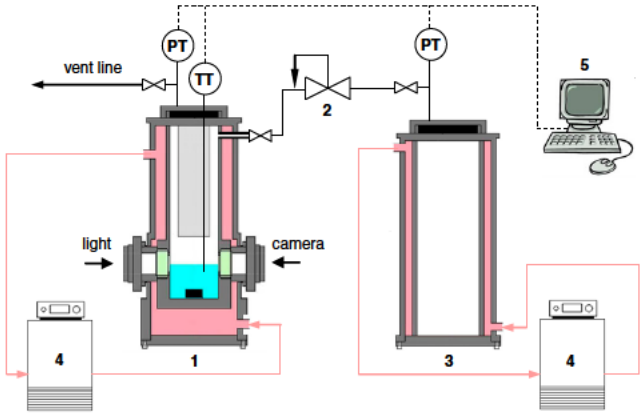

Figure 1. Experimental rig. 1: reactor ; 2: pressure reducing valve ; 3: gas storage vessel ; 4 thermostatic bathes ; 5: computer (PC).

The hydrate formation reactor consists of a titanium cylindrical vessel equipped with two see-through sapphire windows of 20 mm diameter each which allow lighting inside the reactor and making visual observations during hydrate formation. The reactor has a volume of 149 cm^3 and resists pressures up to 200 bar. The reactor is installed on a magnetic stirrer (Hei-Mix D model from Heidolph), and a magnetic agitator of 20 mm diameter can rotate inside the reactor. The reactor is heated and cooled by circulation of an aqueous solution of ethylene glycol into the reactor jacket from a thermostatic bath (Polystat 37, Fisher Scientific). The temperature of the reactor is measured with a PT100 probe plunging into the liquid, the uncertainty of the measurement being ± 0.3 K. The reactor pressure is measured by a KELLER PA23S pressure transducer, 0-200 bar pressure range, with an accuracy of ± 0.5 bar. The reactor is linked to the gas storage vessel with a pressure reducing valve from Dräger-Tescom (pressure range of 0-65 bar) allowing maintaining a constant pressure with a precision of ± 0.1 bar. The whole instrumentation is monitored via a standard PC and a LabView interface, where the temperature and pressure information were sampled every second.

2.3. Protocol

To prepare the solutions containing the additives, SDS is first dissolved in 50 ml of water and this solution is agitated during 5 min. Then, the desired mass of THF is added into the SDS solution and agitated again during 5 min. Finally, the total mass of the solution is adjusted to 200 ± 0.01 g with UPW and maintained under agitation in a glass erlenmeyer closed by a PTFE cap. For all experiments, the reactor is first loaded with 65 ± 0.5 ml of solution using a graduated glass cylinder. This volume has been chosen to have the liquid interface at the middle of the sapphire windows. After the reactor is sealed and connected to the rest of the equipment, the reactor agitation is

started (rotation speed set at 600 rpm) to enhance thermal and mass transfers, and the reactor temperature is regulated to T_{init} = 20.0 °C. Then, with the agitator off, the remaining volume of the reactor and all the loading lines are purged by first increasing the pressure up to 3 bar using CO2, and then venting the reactor until its pressure deceases to 1 bar. To avoid keeping air into the system, this cycle is repeated at least three times. The reactor is then loaded with CO2 at the desired pressure. The agitator is started again and the reactor is maintained at constant pressure and temperature to allow complete CO2 solubilization. After two hours, the reactor is isolated by closing a manual valve and cooled at 0.9 °C/min till 2.0 - 2.5 °C. The temperature is maintained constant at this value till the end of hydrate formation. Due to insufficient agitation torque, the agitator stops immediately when a hydrate phase begins to form: it can be considered here that the hydrate growing is done in quiescent conditions. Finally, the temperature is risen to 20.0 °C to dissociate completely the hydrates formed. Thus, after dissociation, the system returns to its initial levels of pressure and temperature as well as the bulk aspect which is the same than before starting the hydrate formation protocol (a transparent agitated solution).

3. Results

3.1. Example of typical experiment curves

The observed trends of reactor pressure and temperature versus time are qualitatively similar in all experiments. Figure 2(a) shows a type-curve obtained from an initial CO2 pressure in the reactor set to P_{init} = 27.0 bar. The THF and SDS concentrations are equal to 4 wt. % and 3000 ppm, respectively.

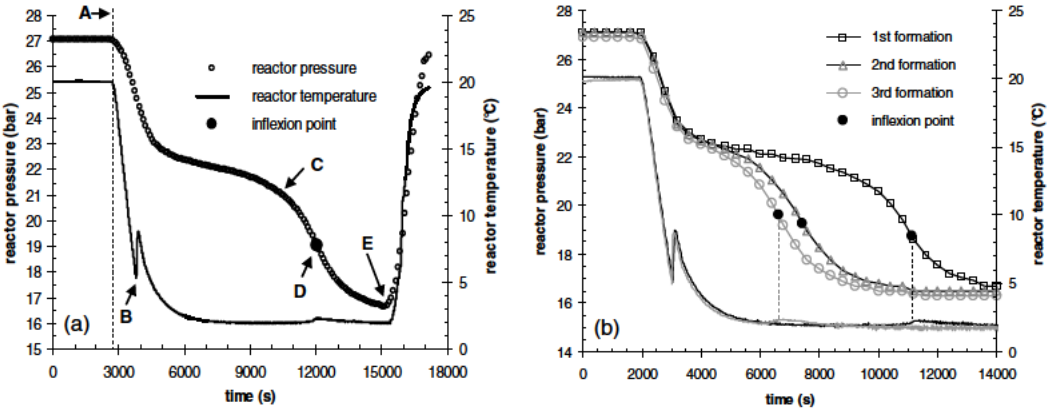

Figure 2. Typical experimental curves with P_{init} = 27.0 bar, [SDS] = 3000 ppm and [THF] = 4 wt. %. (a): reactor pressure and temperature versus time. (b): kinetic curves obtained during successive hydrate formations ; symbols: pressure data ; lines with no symbols: temperature data.

The period from origin to point A represents the end of the CO2 solubilization step in water where both the reactor pressure and temperature are maintained constant at 27.0 bar and 20.0 °C, respectively. At point A, the reactor is isolated from the gas storage vessel and begins to be cooled down to the target temperature (2.2 °C in this example). From point A to B, the pressure in the reactor decreases due to the combined effects of temperature on gas contraction and on CO2 solubility. At point B, a rapid exothermic phenomenon takes place, attributed to a first hydrate crystallisation in the reactor, and a temperature rise of about several degrees in magnitude is measured. When the heat flux released by exothermicity is balanced by the reactor cooling, the temperature decreases again and stabilises at the desired value. After point B, the pressure continues to decrease at slower rate, until point C. This decrease is a combined effect of changes in CO2 solubility in water and CO2 enchlatration. From point C, a dramatic decrease of the reactor pressure is observed corresponding to a higher rate of CO2 consumption,

accompanied with a small temperature peak. The maximum of this exothermic peak corresponds to the pressure curve inflexion point (point D). This period of second hydrate crystallisation, characterized by this strong decrease in pressure, is hereafter called *the high-rate CO2 capture phase*. Then, the pressure curve reaches a pseudo-plateau (just before point E), and the reactor temperature return to the target value, indicating the enclathration reaction reaches its end. In this example, the pseudo-plateau pressure is equal 16.6 ± 0.5 bar, which is very close to the equilibrium pressure for pure CO2 hydrate formation [9]. Therefore, the CO2 capture stops when the reactor pressure reaches the CO2 hydrate equilibrium pressure. Our pressure trends are consistent with those obtained by Liu *et al.* (2008) [17] on the same system, and their final pressure was as well very close to the equilibrium pressure of pure CO2 hydrate. However, these authors did mention neither visual observation nor any exothermicity temperature peak during the reactor cooling step.

Figure 2(b) displays an example of the pressure and temperature curves obtained for a series of three consecutive hydrate formations and dissociations steps carried out with the same initial solution and gas loadings. The initial pressure of 27.0 bar, and the THF and SDS concentrations are 4 wt. % and 3000 ppm, respectively. Between the end of dissociation and the beginning of the subsequent cooling cycle, the system is maintained under agitation at least two hours in order to have comparable temperature and pressure initial conditions. The *overall reaction time* is hereafter defined as the time from the beginning of the reactor cooling to the time when the reactor pressure reaches the single CO2 hydrate equilibrium pressure. As shown in Figure 2(b), the general evolution of the reactor pressure and temperature, the CO2 consumption rate at the inflexion point (slope of the tangent at inflexion point), as well as the final reactor pressure are close for the three experiments. However, some variability is observed in the overall reaction time between successive cooling cycles.

It is well established that CO2 and water form s(I) hydrate structure and single THF forms the structure s(II) hydrate [9]. In the case of a mixed CO2+THF hydrate, its structure is supposed to be s(II) with all the larges cavities occupied by THF and all the small ones by CO2 [12]. Results of Delahaye *et al.* (2006) [18] show that the formation pressure for a mixed THF+CO2 hydrate is significantly lower than for the single CO2 hydrate. At 3 °C, they obtained for a THF-water solution containing 3.8 wt. % of THF (this concentration is close to the concentration used here) a formation pressure of 2.2 bar for the mixed CO2+THF hydrate against 15.3 bar for single CO2 hydrate. Nevertheless, from equilibrium data for water-THF-CO2 ternary systems obtained with THF concentration varying from 1.0 to 16 wt. % and CO2 pressure from 2 to 20 bar, Martinez *et al.* (2008) [12] reported that at sufficient CO2 pressure, the hydrate phases containing CO2 are the more thermodynamically stable phases. Accordingly, the nature of the first solid formed during the reactor cooling is attributed to a hydrate phase containing carbon dioxide, typically a mixed THF-CO2 hydrate. From visual observation through the reactor windows, it is clear that the first crystallisation at point B in Figure 2(a) takes place within the entire bulk of the water phase. The structure of this dispersion is likely to strongly influence the CO2 mass transfer processes, and consequently, the hydrate formation kinetics.

The high-rate CO2 capture phase is likely to correspond to the formation of single CO2 hydrate. In addition, as hydrates are non stoechiometric compounds, the hydration number of pure CO2 hydrate has been reported to be higher than the theoretical value of 5.75 and a value of $N_H^{single} = 7.30 \pm 0.13$ [8] can be considered here. In the case of a mixed CO2+THF hydrate, the lowest hydration number is 8.5 and the theoretical formula of the mixed hydrate is CO2-0.5THF-8.5H2O [19]. However, this hydration number depends on the CO2 pressure and was found to be close to around 20 with $P_{CO2} = 21$ bar [12]. Consequently, for the same mass of water used for forming the hydrates, a much larger CO2 quantity is stored in the pure CO2 hydrate in comparison to the mixed CO2+THF hydrate.

3.2. Effects of THF and SDS concentrations

It is proposed here to evaluate whether and how the high-rate CO2 capture phase varies when the concentration of THF or SDS is modified.

The effect of THF concentration was studied with an initial pressure of 27.0 bar and a concentration of SDS equal to 3000 ppm. A minimum of three runs (hydrate formation) was done for each concentration. The results obtained for five THF concentrations ranging from 0.5 to 4 wt. % are presented in Figure 3.

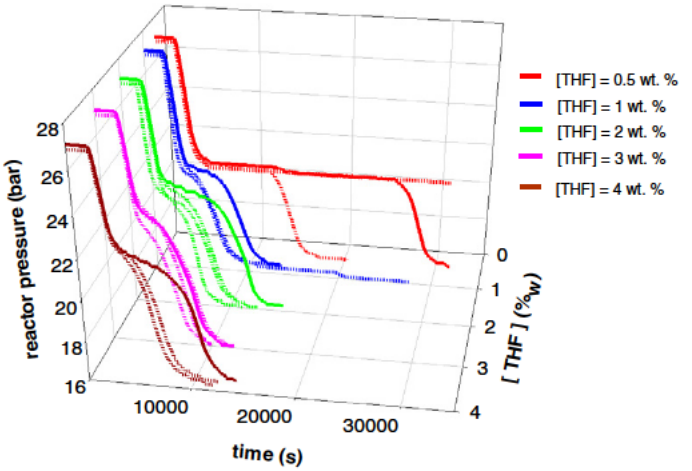

Figure 3. 3D plot showing the influence of THF concentration on the CO2 capture kinetics. Full lines correspond to first hydrate formation (by opposition to dotted lines). Conditions are P_{init} = 27.0 bar ; [SDS] = 3000 ppm.

As mentioned above, the reactor pressure sharply decreases when CO2 begins to be captured at high rate. The kinetic curves presented in Figure 3 show that the high-rate CO2 capture phase are observed for all concentrations tested. However, from 1 to 4 wt. %, the overall reaction time has been found to be in the same order of magnitude. For the smallest THF concentration of 0.5 wt. %, the reactor pressure is observed to stabilise firstly to a constant pressure level and then, in two of the three experiments carried out, pressure drops sharply. Some additional experimental and modelling works are underway to clarify how this pressure level is linked to the solubility equilibrium. For one of these three experiments, both the first temperature peak and the high-rate capture phase have not been observed within 35000 seconds. Thus, a THF concentration of 0.5 wt. % may be near a limit value which allows the promoting effects on hydrate formation, and a THF concentration superior or equal to 1 wt. % appears to be well adapted for these experimental conditions.

The influence of SDS concentration has been studied with an initial CO2 pressure of 27.0 bar and a THF concentration equal to 4 wt. %. Figure 4(a) shows the evolution of the reactor pressure vs. time for different SDS concentrations from 0 to 5000 ppm. All data in this figure correspond to the first hydrate formation (no cycle).

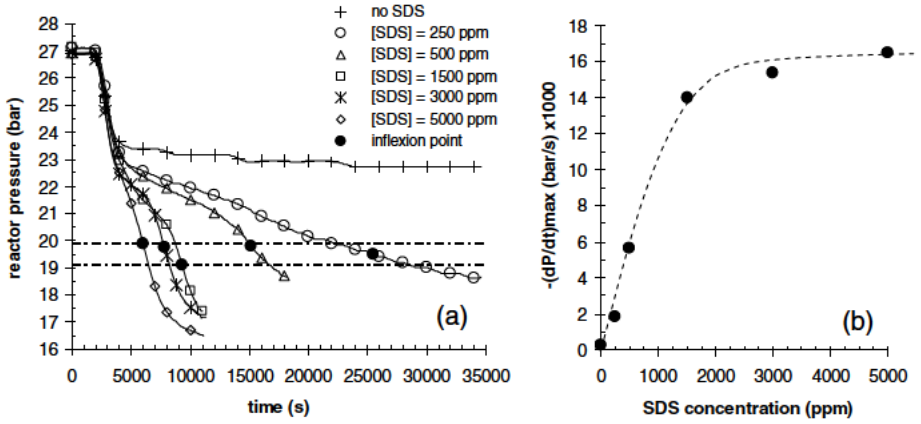

Figure 4. Influence of SDS concentration on CO2 capture. (a): Kinetic curves. (b) $(dP/dt)_{max}$ function of SDS concentration. Black dots represent inflexion points of the pressure curves after the reactor temperature has reached the temperature target. P_{init} = 27.0 bar, [THF] = 4 wt. %.

The overall reaction time was found to be directly dependent on SDS concentration. However, for SDS concentrations above 1500 ppm, the overall reaction time can be considered in the same order of magnitude as some variability is observed. This variability is shown in Figure 2(b) by the variation in the position of inflexion points obtained for three successive experiments carried out with [SDS] = 3000 ppm. However, the pressures obtained at inflexion points are located in a narrow interval from 19.1 to 19.9 bar (P_{inflex}^{mean} = 19.6 bar). This result indicates that the maximum capture rate is strongly dependent on the value of the reactor pressure. The experiment conducted with only 4 wt. % THF with no SDS shows a very slow CO2 consumption (pressure remains almost constant). In these conditions, although the first temperature peak (attributed to the formation of a mixed CO2-THF hydrate) is detected and the hydrate formation within the bulk is clearly visible, the high-rate CO2 capture phase is not observed, suggesting a strong coupling between the THF and SDS effects. Figure 4(b) shows (dP/dt) values at inflexion points (named $(dP/dt)_{max}$) vs. SDS concentration. It appears from Figure 4(b) that the capture rate, which is proportional to dP/dt, increases with (low) SDS concentration, and then it levels off to a constant value when the SDS concentration exceeds about 1500 ppm. In addition, we have carried out experiments with only SDS or only THF and, similarly to Liu *et al.* (2008) [17], we did not observe the high-rate CO2 capture phase. Thus, A SDS concentration superior of equal to 1500 ppm appears to be well adapted in these conditions.

4. Conclusion and prospects

A series of batch experiments under quiescent conditions has been undertaken showing that SDS and THF used in combination are efficient additives for enhancing CO2 capture. The presence of these two water-soluble additives in suitable concentrations ([SDS] ≥ 1500 ppm and 1 wt. % ≤ [THF] ≤ 4 wt. %) is necessary to have a high-rate CO2 capture. Our observations support the following mechanism. First, mixed CO2+THF hydrates are formed in the bulk of the water solution. These hydrates, which are stable initially due to high CO2 pressure, then become unstable when the reactor pressure decreases down to the pressure where the CO2 hydrate phase is more stable. In the second step, pure CO2 hydrate forms. An important role is certainly played by the initial dispersion of mixed hydrates (specific area, enhanced mass transfers, etc) and further studies are ongoing to better characterize these mechanisms. In particular, thermodynamic models are being developed to make the difference between the CO2 quantity which dissolves into the remaining interstitial water (pure solubility effect), and the CO2 which is enclathrated into hydrates. We are currently testing this mixture of additives (and others similar additives) with CO2-rich gas mixtures, both on kinetic and selectivity points of view with the purpose to develop an economical and competitive hydrate-based CO2 capture process.

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